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Conversion of Oil Palm Empty Fruit Bunch to Biofuels

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1. Introduction

Crude palm oil production is reaching 48.99 million metric tonnes per year globally in 2011 and Southeast Asia is the main contributor, with Indonesia accounting for 48.79%, Malaysia 36.75%, and Thailand 2.96% (Palm Oil Refiners Association of Malaysia, 2011). Oil palm is a multi-purpose plantation and it is also an intensive producer of biomass. Accompanying the production of one kg of palm oil, approximately 4 kg of dry biomass are produced. One third of the oil palm biomass is oil palm empty fruit bunch (OPEFB) and the other two thirds are oil palm trunks and fronds [1-3].



Figure 1. Oil palm and oil palm empty fruit bunch.

The supply of oil palm biomass and its processing by-products are found to be seven times that of natural timber [4]. Besides producing oils and fats, there are continuous interests in using oil palm biomass as the source of renewable energy. Among the oil palm biomass, OPEFB is the most often investigated biomass for biofuel production. Traditionally, OPEFB is used for power and steam utilization in the palm oil mills, and is used for composting and soil mulch. Direct burning of OPEFB causes environmental problems due the incomplete combustion and

the release of very fine particles of ash. The conversion of OPEFB to biofuels, such as syngas, ethanol, butanol, bio-oil, hydrogen and biogas etc., might be a good alternative and have less environmental footprint. The properties of OPEFB is listed in Table 1 [5].

	Literature values	Measured	
	% (w/w)	% (w/w)	Method
Components			
Cellulose	59.7	na	na
Hemicellulose	22.1	na	na
Lignin	18.1	na	na
Elemental analysis			
Carbon	48.9	49.07	Combustion analysis
Hydrogen	6.3	6.48	
Nitrogen	0.7	0.7	
Sulphur	0.2	<0.10	
Oxygen	36.7	38.29	By difference
K	2.24	2.00	Spectrometry
K ₂ O	3.08–3.65	na	na
Proximate analysis			
Moisture	na	7.95	ASTM E871
Volatiles	75.7	83.86	ASTM E872
Ash	4.3	5.36	NREL LAP005
Fixed carbon	17	10.78	By difference
HHV (MJ/kg)	19.0	19.35	Bomb calorimeter
LHV (MJ/kg)	17.2	na	na

Notes: na - not available.

Table 1. Properties of oil palm empty fruit bunch

While all the OPEFB components can be converted to biofuels, such as bio-oil and syngas through thermo-chemical conversion, cellulose and hemicellulose can be hydrolysed to sugars and subsequently be fermented to biofuels such as ethanol, butanol, and biogas etc. Although many scientists around the world are developing technologies to generate biofuels from OPEFB, to-date, none of such technologies has been commercialized. This is largely due to the recalcitrance of the OPEFB and therefore the complexity of the conversion technologies making biofuels from OPEFB less competitive than the fossil-based fuels. Continual efforts in R&D are still necessary in order to bring such technology to commercialization. The aim of this paper is to review the progress and challenges of the OPEFB conversion technologies so as to help expedite the OPEFB conversion technology development.

2. Pretreatment

Similar to all other lignocellulosic biomass, OPEFB are composed of cellulose, hemicellulose and lignin. Among the three components, lignin has the most complex structure, making it recalcitrant to both chemical and biological conversion. Pretreatment of OPEFB is therefore necessary to open its structure and increase its digestibility and subsequently the degree of conversion. Pretreatment of OPEFB can be classified as biological pretreatment, physical pretreatment, chemical pretreatment, and physical-chemical pretreatment.

For biological pretreatment, oxidizing enzymes and white-rot fungi were used to degrade the lignin content in OPEFB. For example, enzymes such as lignin peroxidase (LiP) and manganese peroxidase (MnP) was used to pretreat OPEFB for fast pyrolysis and the bio-oil yield was improved from 20% to 30% [6]. Syafwina et al. used white-rot fungi to pretreat OPEFB and the saccharification efficiency was improved by 150% compared to that of the untreated OPEFB [7].

Among all the pretreatment methods, chemical pretreatment is most often reported for OPEFB. Two-stage dilute acid hydrolysis [8], alkali pretreatment [9], sequential dilute acid and alkali pretreatment [10], alkali and hydrogen peroxide pretreatment [11], sequential alkali and phosphoric acid pretreatment [10], aqueous ammonia [12], and solvent digestion [5] were used to increase the digestibility of OPEFB. Among all the chemical methods investigated, alkali pretreatment seemed to be the most effective. Umikalsom et al. autoclaved the milled OPEFB in the presence of 2% NaOH and 85% hydrolysis yield was obtained [13]. Han and his colleagues investigated NaOH pretreatment of OPEFB for bioethanol production [9]. The optimal conditions were found to be 127.64°C, 22.08 min, and 2.89 mol/L NaOH. With a cellulase loading of 50 FPU /g cellulose a total glucose conversion rate (TGCR) of 86.37% was obtained using the Changhae Ethanol Multi Explosion (CHEMEX) facility. The effectiveness of alkali pretreatment might be attributed to its capability in lignin degradation. Mission et al. investigated the alkali treatment followed H₂O₂ treatment and found that almost 100% lignin degradation was obtained when OPEFB was firstly treated with dilute NaOH and subsequently with H₂O₂ [11]. This confirmed the lignin degradation by NaOH and its enhancement by the addition of H₂O₂.

Besides alkali pretreatment, physical-chemical pretreatment such as ammonium fibre explosion (AFEX) [14] and superheated steam [15] were also shown to be effective in the increase of OPEFB digestibility. Hydrolysis efficiency of 90% and 66% were obtained, respectively.

3. Thermo-chemical conversion

Thermo-chemical conversion is one of the important routes to obtain fuels from lignocellulosic biomass. Thermo-chemical conversion of biomass involves heating the biomass materials in the absence of oxygen to produce a mixture of gas, liquid and solid. Such products can be used as fuels after further conversion or upgrading. Generally, thermo-chemical processes

have lower reaction time required (a few seconds or minutes) and the superior ability to destroy most of the organic compounds. These mainly include biomass pyrolysis and biomass gasification. Recently, thermo-chemical pretreatment of biomass, such as torrefaction was introduced to upgrade biomass for more efficient biofuel production [16-17].

3.1. OPEFB pyrolysis

Pyrolysis is defined as the thermal degradation of the biomass materials in the absence of oxygen. It is normally conducted at moderate temperature (400 – 600°C) over a short period of retention time. Its products comprise of liquids (water, oil/tars), solids (charcoal) and gases (methane, hydrogen, carbon monoxide and carbon dioxide). The efficiency of pyrolysis and the amount of solid, liquid, and gaseous fractions formed largely depend on the process parameters such as pretreatment condition, temperature, retention time and type of reactors.

Misson et al investigated the effects of alkaline pretreatment using NaOH, $\text{Ca}(\text{OH})_2$, in conjunction with H_2O_2 , on the catalytic pyrolysis of OPEFB [11]. They proved that consecutive addition of NaOH and H_2O_2 decomposed almost 100% of OPEFB lignin compared to 44% for the $\text{Ca}(\text{OH})_2$ and H_2O_2 system, while the exclusive use of NaOH and $\text{Ca}(\text{OH})_2$ could not alter lignin composition much. In addition, the pretreated OPEFB was catalytically pyrolysed more efficiently than the untreated OPEFB samples under the same conditions.

Fast pyrolysis represents a potential route to upgrade the OPEFB waste to value-added fuels and renewable chemicals. For woody feedstock, temperatures around 400-600°C together with short vapour residence times (0.5-2 s) are used to obtain bio-oil yields of around 70%, along with char and gas yields of around 15% each. Sulaiman and Abdullah investigated fast pyrolysis of OPEFB using and bench top fluidized bed reactor with a nominal capacity of 150 g/L [18]. After extensive feeding trials, it was found that only particles between 250 and 355 μm were easily fed. The maximum liquid and organics yields (55% total liquids) were obtained at 450°C. Higher temperature was more favourable for gas production and water content was almost constant in the range of temperature investigated. The maximum liquids yield and the minimum char yield were obtained at a residence time of 1.03 s. The pyrolysis liquids produced separated into two phases; a phase predominated by tarry organic compounds (60%) and an aqueous phase (40%). The phase separated liquid product would represent a challenging fuel for boilers and engines, due to the high viscosity of the organics phase and the high water content of the aqueous phase. These could be overcome by upgrading. However, the by-product, charcoal, has been commercialized for quite some time. It is worth noting that the first pilot bio-oil plant by Genting Bio-oil has already started operation in Malaysia [19].

3.2. OPEFB gasification

Gasification process is an extension of the pyrolysis process except that it is conducted at elevated temperature range of 800–1300 °C so that it is more favourable for gas production [20]. The gas stream is mainly composed of methane, hydrogen, carbon monoxide, and carbon dioxide. Biomass gasification offers several advantages, such as reduced CO_2 emissions,

compact equipment requirements with a relatively small footprint, accurate combustion control, and high thermal efficiency. The main challenge in gasification is enabling the pyrolysis and gas reforming reactions to take place using the minimum amount of energy and gasifier design is therefore important [21].

Ogi et al. used an entrained-flow gasifier for OPEFB gasification at 900°C [22]. During gasification with H₂O alone, the carbon conversion rate was greater than 95% (C-equivalent), and hydrogen-rich gas with a composition suitable for liquid fuel synthesis ([H₂]/[CO] = 1.8–3.9) was obtained. The gasification rate was improved to be greater than 99% when O₂ was added to H₂O; however, under these conditions, the gas composition was less suitable for liquid fuel synthesis due to the increase of CO₂ amount. Thermogravimetric (TG) analysis suggested that OPEFB decomposed easily, especially in the presence of H₂O and/or O₂, suggesting that OPEFB is an ideal candidate for biomass gasification. Lahijani and Zainal investigated OPEFB gasification in a pilot-scale air-blown fluidized bed reactor [23]. The effect of bed temperature (650–1050°C) on gasification performance was studied and the gasification results were compared to that of sawdust. Results showed that at 1050°C, OPEFB had almost equivalent gas yield and cold gas efficiency compared with saw dust, however, with low maximal heating values and higher carbon conversion. In addition, it was realized that agglomeration was the major issue in OPEFB gasification at high temperatures. This can be overcome by lowering the temperature to 770 ± 20 °C. Mohammed et al. studied OPEFB gasification in a bench scale fluidized-bed reactor for hydrogen-rich gas production [24]. The total gas yield was enhanced greatly with the increase of temperature and it reached the maximum value (~92 wt.%) at 1000 °C with big portions of H₂ (38.02 vol.%) and CO (36.36 vol.%). The feedstock particle size of 0.3–0.5 mm, was found to obtain a higher H₂ yield (33.93 vol.%), and higher LHV of gas product (15.26 MJ/m³). The optimum equivalence ratio (ER) (0.25) was found to attain a higher H₂ yield (27.31 vol.%) at 850 °C. Due to the low efficiency of bench scale gasification unit the system needs to be scaling-up. The cost analysis for scale-up EFB gasification unit showed that the hydrogen supply cost is \$2.11/kg OPEFB. Recently, a characterization and kinetic analysis was done by Mohammed et al. and it was found that a high content of volatiles (>82%) increased the reactivity of OPEFB, and more than 90% decomposed at 700 °C; however, a high content of moisture (>50%) and oxygen (>45%) resulted in a low calorific value [25]. The fuel characteristics of OPEFB are comparable to those of other biomasses and it can be considered a good candidate for gasification.

3.3. OPEFB torrefaction

Torrefaction is a thermal conversion method of biomass in the low temperature range of 200–300 °C. Biomass is pretreated to produce a high quality solid biofuel that can be used for combustion and gasification [16–17]. It is based on the removal of oxygen from biomass to produce a fuel with increased energy density. Different reaction conditions (temperature, inert gas, reaction time) and biomass resources lead to the differences in solid, liquid and gaseous products.

Uemura et al. [16] studied the effect of torrefaction on the basic characteristics of oil palm empty fruit bunches (EFB), mesocarp fibre and kernel shell as a potential source of solid fuel. It was

found that mesocarp fibre and kernel shell exhibited excellent energy yield values higher than 95%, whereas OPEFB, on the other hand, exhibited a rather poor yield of 56%. Torrefaction can also be done in the presence of oxygen. Uemura and his colleagues [17] carried out OPEFB torrefaction in a fixed-bed tubular reactor in the presence of oxygen at varied oxygen concentration. The mass yield decreased with increasing temperature and oxygen concentration, but was unaffected by biomass particle size. The energy yield decreased with increasing oxygen concentrations, however, was still between 85% and 95%. It was found that the oxidative torrefaction process occurred in two successive steps or via two parallel reactions, where one reaction is ordinary torrefaction, and the other is oxidation.

3.4. Summary

The analysis of thermo-chemical conversion of OPEFB suggests that gasification is the most suitable thermo-chemical route for OPEFB conversion to biofuels. It has the highest carbon conversion (>90%) and biofuel yield. Due to the high viscosity and high water content of pyrolysis products, application of bio-oil as a biofuel is still very challenging. Compared to other oil palm residues, such as oil palm kernel, due to its high water content, OPEFB may not be a good candidate for solid fuels even after torrefaction pretreatment.

4. Bioconversion

Bioconversion of lignocellulosic biomass to fuels involves three major steps: 1) pretreatment to effectively broken the biomass structure and release the biomass components i.e. cellulose, hemicellulose, and lignin, and therefore increase the digestibility of the biomass; 2) enzymatic hydrolysis – to hydrolyse cellulose and hemicellulose and produce fermentable sugar, such as glucose, xylose etc.; 3) fermentation – to convert the biomass hydrolysate sugars to the desired products. OPEFB was intensively investigated as a potential substrate for the production of biofuels, such as ethanol, butanol, and biogas etc. Among the biofuels produced through bioconversion of OPEFB, cellulosic ethanol is the most intensively studied.

Two stage dilute acid hydrolysis was applied for OPEFB bioconversion to ethanol, 135.94 g xylose/kg OPEFB and 62.70 g glucose/kg OPEFB were produced in the first stage and 2nd stage, respectively [8]. They were then fermented to ethanol using *Mucor indicus* and *Saccharomyces cerevisiae*, respectively, and the corresponding ethanol yields were 0.45 and 0.46 g ethanol/g sugar.

Alkali is the most often used pretreatment chemical for cellulosic ethanol production from OPEFB. Kassim et al. pretreated OPEFB using 1% NaOH followed by mild acid (0.7% H₂SO₄) hydrolysis and enzymatic saccharification [26]. A total of 16.4 g/L of glucose and 3.85 g/L of xylose were obtained during enzymatic saccharification. The OPEFB hydrolysate was fermented with *Saccharomyces cerevisiae* and an ethanol yield of 0.51 g/g yield was obtained, suggesting that OPEFB is a potential substrate for cellulosic ethanol production. Han and his colleagues investigated ethanol production through pilot scale alkali pretreatment and fermentation [9]. The best pretreatment condition was 127.64 °C, 22.08 min, and 2.89 mol/L

NaOH. Enzyme loading of 50 FPU/g cellulose resulted in 86.37% glucose conversion in their Changhae Ethanol Multi Explosion (CHEMEX) facility. An ethanol concentration of 48.54 g/L was obtained at 20% (w/v) pretreated biomass loading, along with simultaneous saccharification and fermentation (SSF) processes. This is so far the highest reported ethanol titre from OPEFB. Overall, 410.48 g of ethanol were produced from 3 kg of raw OPEFB in a single run, using the CHEMEX 50 L reactor.

Jung and his colleagues tried aqueous ammonia soaking for the pretreatment of OPEFB and its conversion to ethanol [12]. Pretreated OPEFB at 60°C, 12 h, and 21% (w/w) aqueous ammonia, showed 19.5% and 41.4% glucose yields after 96h enzymatic hydrolysis using 15 and 60 FPU of cellulase per gram of OPEFB, respectively. An ethanol concentration of 18.6 g/L and a productivity of 0.11 g/L/h were obtained with the ethanol yield of 0.33 g ethanol/glucose.

Lau et al. successfully applied ammonia fibre expansion (AFEX) pretreatment for cellulosic ethanol production from OPEFB [14]. The sugar yield was close to 90% after enzyme formulation optimization. Post-AFEX size reduction is required to enhance the sugar yield possibly due to the high tensile strength (248 MPa) and toughness (2,000 MPa) of palm fibre compared to most cellulosic feedstock. Interestingly, the water extract from AFEX-pretreated OPEFB at 9% solids loading is highly fermentable and up to 65 g/L glucose can be fermented to ethanol within 24 h without the supplement of nutrients.

OPEFB was also used for butanol production. Noomtim and Cheirsilp (2011) studied butanol production from OPEFB using *Clostridium acetobutylicum* [27]. Again, the pretreatment by alkali was found to be the most suitable method to prepare OPEFB for enzymatic hydrolysis. 1.262 g/L ABE (acetone, butanol and ethanol) was obtained in RCM medium containing 20 g/L sugar obtained from cellulase hydrolysed OPEFB. Ibrahim et al also investigated OPEFB as the potential substrate for ABE production [28]. Higher ABE yield was obtained from treated OPEFB when compared to using a glucose-based medium using *Clostridium butyricum* EB6. A higher ABE level was obtained at pH 6.0 with a concentration of 3.47 g/L. The accumulated acid (5 to 13 g/L) had inhibitory effects on cell growth.

Nieves et al. investigated biogas production using OPEFB. OPEFB was pre-treated using NaOH and phosphoric acid [29]. When 8% NaOH (60 min) was used for the pretreatment, 100% improvement in the yield of methane production was observed and 97% of the theoretical value of methane production was achieved under such pretreatment condition. The results showed that the carbohydrate content of OPEFB could be efficiently converted to methane under the anaerobic digestion process. O-Thong et al. investigated the effect of pretreatment methods for improved biodegradability and biogas production of oil palm empty fruit bunches (EFB) and its co-digestion with palm oil mill effluent (POME) [30]. The maximum methane potential of OPEFB was 202 mL CH₄/g VS-added corresponding to 79.1 m³ CH₄/ton OPEFB with 38% biodegradability. Co-digestion of treated OPEFB by NaOH pre-soaking and hydrothermal treatment with POME resulted in 98% improvement in methane yield comparing with co-digesting untreated OPEFB. The maximum methane production of co-digestion treated OPEFB with POME was 82.7 m³ CH₄/ton of mixed treated OPEFB and POME (6.8:1), corresponding to methane yield of 392 mL CH₄/g VS-added. The study

showed that there was a great potential to co-digestion treated OPEFB with POME for bio-energy production.

In summary, OPEFB has been frequently investigated as a substrate for biofuel production through bioconversion. Cellulosic ethanol production was most intensively investigated and the highest ethanol titre of 48.54 g/L was obtained through alkali pretreatment in a pilot scale reactor [9]. Although not much research has been done for ABE and biogas production, the few reports summarized in this paper suggest that OPEFB is also potential substrate for butanol and biogas production. Throughout the reports reviewed, alkali-based pretreatment methods, such as NaOH alone, NaOH followed by acid, and ammonium fibre expansion (AFEX) pretreatment are the most effective in enhancing OPEFB digestibility.

5. Conclusion

In conclusion, OPEFB is the most potential renewable resource for biofuel production in South-east Asia. It can be converted to biofuels through thermo-chemical or biological conversion. Pretreatment of OPEFB is necessary for both routes of conversion and alkali pretreatment is the most effective. A summary of OPEFB conversion technology is shown in Fig. 2.

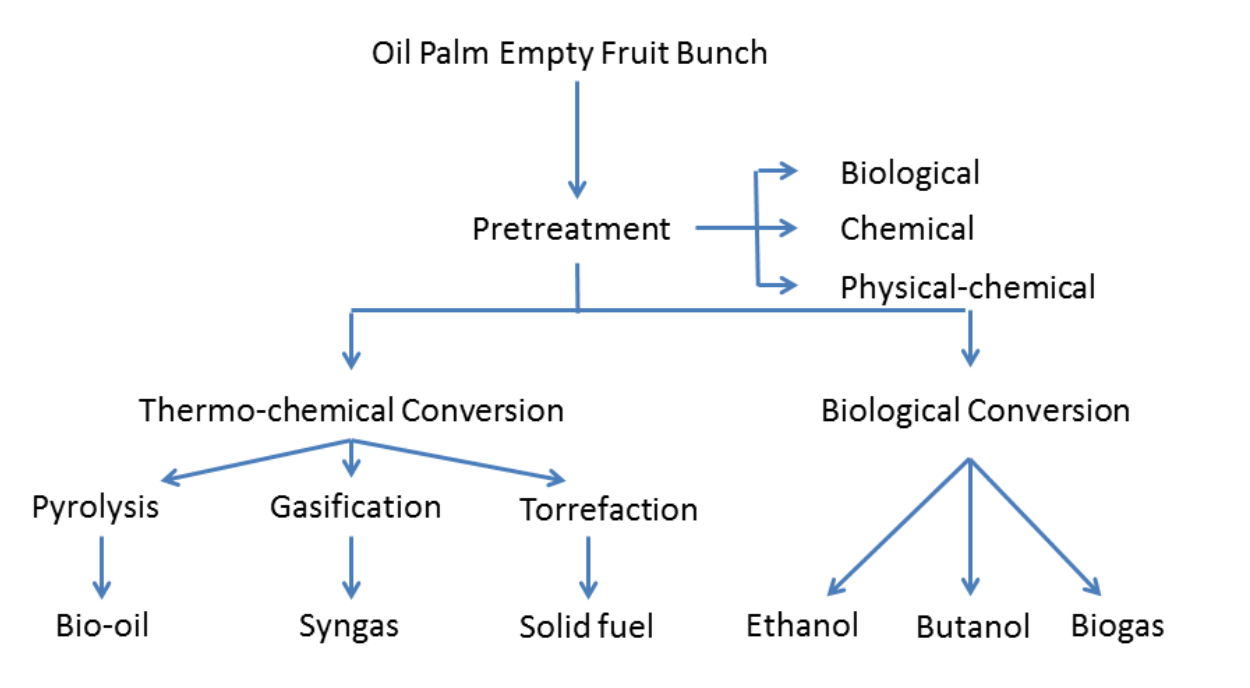


Figure 2. Biofuel production from OPEFB.

Among the studies on OPEFB thermo-chemical conversion, it seems that gasification is the most suitable approach to obtain bioenergy from OPEFB and has potential in commerciali-

zation. Pyrolysis, on the other hand, produced very complex bio-oil with high viscosity and water content, making it challenging for commercialization. However, charcoal from OPEFB pyrolysis can be a potential commercial product. Compared to other palm oil residues, such as oil palm kernel, OPEFB may not be a good candidate for solid fuel production, even after torrefaction pretreatment due to its high water content and low energy capacity.

Biological conversion of OPEFB is another route to obtain biofuels from OPEFB. Cellulosic ethanol production was most intensively studied and around 50 g/L titre was obtained with 20% (w/v) biomass loading through NaOH pretreatment. AFEX also showed potential in OPEFB pretreatment and a glucose yield of 90% was obtained with 9% biomass loading. The water extract of the AFEX pretreated OPEFB was highly fermentable. OPEFB also showed some promising preliminary results in ABE (acetone, butanol and ethanol) and biogas production; however, further investigation is necessary to enhance OPEFB conversion potentials in these areas.

For both thermo-chemical and biological conversion of OPEFB, pretreatment technology is the key for the process cost. Although alkali pretreatment is effective, scaling-up the process requires huge amount of acid to neutralize the base in the pretreatment solution. In addition, before alkali pretreatment, OPEFB should be milled to reduce its size, which is energy-consuming. Steam explosion is effective for a lot of lignocellulosic biomass, however not much research was found on its pretreatment of OPEFB. A cost-effective pretreatment is the key for the successful commercialization of OPEFB conversion technologies for biofuel production.

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